NAPHTHAZARIN COMPLEXES OF THORIUM AND RARE EARTH METAL IONS

BY

MELVIN TECOTZKY

B.S., University of Illinois, 1948

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

Solutions of thorium salts show no absorption in the range 2000 - 10,000 A, thus thorium cannot be identified by direct absorption spectra measurements (3). Formanek (1) has shown that when the dye alkannin is added to thorium salt solutions, one obtains a violet solution showing maximum absorption in the range 6055 - 6084 A.

Recently, in seeking a more satisfactory method for the determination of beryllium, Underwood and Neuman (5) developed a method first using alkannin and then an equivalent procedure using naphthazarin (5,8-dihydroxy-1,4-naphthoquinone). Since alkannin is a substituted naphthazarin, the two compounds would be expected to behave similarly. These recent investigations of the naphthazarin complexes of beryllium have indicated that a study of the reactions of other metal ions with this reagent might prove fruitful. Inasmuch as there is a lack of color reactions for thorium and the rare earth metal ions, it seemed logical to investigate the reactions of naphthazarin with these ions from this point of view.

Experimental And Discussion

1. The Reagent

Naphthazarin is prepared by the Friedel-Crafts Reaction of hydroquinone and maleic anhydride (4). The product is recrystallized from high boiling petroleum ether and is obtained as brown needles.

When dissolved in an organic solvent such as dioxane or ethanol, naphthazarin produces a red solution. Upon the addition of various metal ions the color of the solution changes, the color change being from red to reddish blue or violet. Absolute ethanol has been used as a solvent for naphthazarin

in this investigation. Metal ions have been used as aqueous solutions of their nitrate or chloride salts.

Upon the addition of a solution of thorium nitrate to a naphthazarin solution, there is a distinct color change from red to violet or purple, due to the formation of a thorium-naphthazarin complex. Solutions containing as little as 1×10^{-3}mg. of thorium ion per ml. give visible evidence of complex formation. The color produced by rare earth metal ions with naphthazarin is a deeper red than that of the naphthazarin alone. The color change produced by rare earth metal ions is not as pronounced as the color change produced by thorium ion.

2. Absorption Spectra of the Thorium-Naphthazarin Complex

The absorption spectrum of naphthazarin in ethanol is characterized by twin absorption peaks at 4875 A and 5166 A and by an inflection point at 5500 A. The spectrum of the thorium-naphthazarin complex is also characterized by two absorption peaks. The first appears at 5700 A and the second appears at 6185 A. This spectrum also has a point of inflection at 5375 A. The spectrum of the complex is sufficiently different from that of the uncomplexed reagent to permit a study of the complex by spectrophotometric techniques.

Absorption spectra measurements were made with the Beckman D U Quartz Spectrophotometer and the Cary Recording Spectrophotometer. Only one colored complex species was found to be present in solution.

3. The Composition of the Complex

An attempt to elucidate the empirical formula of the thorium-naphthazarin complex was made through the use of the method of Continuous Variations (2,6). Use was made of the difference in optical density between a naphthazarin solution and a solution of the complex of the same molarity. This difference in optical density, known as Y, between the complexed and uncomplexed reagent was plotted against con-

centration. The molar ratio where Y is a maximum is the molar ratio of the complex. When the values obtained were plotted, the maximum appeared at 34% thorium and 66% naphthazarin. This indicates a two to one complex, two naphthazarin molecules to one thorium atom.

Further agreement with this result was obtained by the application of the Molar Ratio Method. It has been reported by Yoe and Jones (7) that for a very stable complex, a plot of optical density against molar ratio of component *B* to component *A*, with *A* constant, rises from the origin as a straight line and breaks sharply to constant optical density at the molar ratio of the components in the complex. The curve obtained broke at a ratio of four moles of naphthazarin to two moles of thorium. This indicates a two to one complex.

4. Stability of the Complex

A stability study of the thorium-naphthazarin complex over a period of forty-three days indicated a very small change in optical density over this period of time. The complex appears to be stable enough in solution to work with for normal intervals of time without appreciable decomposition. When the complex was exposed to the direct rays of the sun, a much more rapid decomposition was found to take place. The absorption due to the complex was shifted to shorter wavelengths, and there was a considerable decrease in optical density.

5. Colloidal Properties of the Complex

The complex species in solution will migrate to the cathode of a cell under the influence of an electric current. This indicates the presence of a positive charge on the complex in solution. Upon the addition of ammonium hydroxide to a violet thorium-naphthazarin solution, containing excess thorium, a precipitate of thorium hydroxide forms. Upon agitation the solution becomes colorless and the precipitate becomes violet in color. If an excess of naphthazarin is present the

precipitate forms and the resulting solution is blue in color. Naphthazarin is blue in a basic solution. The thorium-naphthazarin material becomes adsorbed on the thorium hydroxide precipitate, in a manner similar to the adsorption of aluminon reagent on an aluminum hydroxide precipitate. The thorium-naphthazarin complex is flocculated by strong electrolytes and will not pass through a dialyzing membrane.

6. Adherence to Beer's Law

Various studies of the adherence to Beer's Law of solutions of the thorium-naphthazarin complex have been made. When the solutions prepared contained less than a two to one ratio of naphthazarin to thorium, no adherence to Beer's Law was found to exist. When, however, the ratio of naphthazarin to thorium was two to one or greater, the solution of the complex was found to adhere to Beer's Law in the range 10^{-6} moles/l. This adherence to Beer's Law is important since it may provide a method for the quantitative determination of thorium.

7. The Rare Earth-Naphthazarin Complex

The absorption spectra of solutions of lanthanum, praseodymium, neodymium, samarium, gadolinium, erbium, and yttrium ions combined with naphthazarin were examined with the Cary Recording Spectrophotometer. The spectra obtained were all similar. The characteristic peak for the rare earth-naphthazarin complex is located between 6000 and 6065 A. This is over 100 A from the thorium-naphthazarin peak.

Since the rare earth metal ions are similar in their chemical behavior, two rare earth metal ions were chosen as typical for further study. A two to one complex was found to form between naphthazarin and praseodymium and naphthazarin and erbium. Both of these complexes were found to adhere to Beer's Law in the range of 10^{-6} mole/l.

The determination of thorium in the presence of excess rare earth metal ion, through the use of naphthazarin, has been attempted. No success was achieved in the presence of

excess rare earth metal ion.

8. Absorption Spectra of Naphthazarin With Other Metal Ions

The absorption spectra of the uranyl, zirconyl, and titanyl naphthazarin complexes were all found to be similar to the rare earth and thorium naphthazarin spectra.

9. Possible Structure of the Complex

Although no definite structure can be given for the naphthazarin metal complexes formed in solution, some suggestions may be made. It appears that the complex may be polymeric in nature. The metal ion is probably bound between two naphthazarin molecules in a chelate type structure. This does not satisfy the oxidation number of the metal and leaves an overall charge on the species in solution. It was not possible to obtain a consistent result for the stability constant of the thorium-naphthazarin complex.

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VITA

Melvin Tecotzky was born on February 17, 1924 in Chicago, Illinois. He received his primary and secondary education in the public schools of that city. After his graduation from Parker High School in 1942, he entered Wilson Junior College in Chicago. After the completion of one year at Wilson Junior College, he volunteered for induction into the United States Air Force in January 1943. He was later transferred to the A. S. T. P. Program at Colorado A. and M. In February 1944 the A. S. T. P. Program was discontinued and the author was transferred to the 97th Infantry Division. He served with the 97th Division in the American, European, and Pacific Theaters of Operations. Following his honorable discharge from the army in 1946, he entered the University of Illinois and received the degree of Bachelor of Science in June 1948.

In September of 1948, he entered the University of Kansas, where he held a part time teaching assistantship in the Department of Chemistry. In February of 1950 he entered the Graduate College of the University of Illinois. During the academic years of 1951-1952 and 1952 to June 1953 he held a research assistantship, sponsored by E. I. duPont de Nemours and Company. During the summer of 1951, he was employed in the Ceramic Laboratory of the United States Steel Company in Chicago, Illinois.

The author is a member of the Chemical Society, the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Alpha Chi Sigma, and Alpha Epsilon Pi.